

ALTERATION OF CLAY MINERALS AND ZEOLITES IN HYDROTHERMAL BRINES

SRIDHAR KOMARNENI AND DELLA M. ROY

Materials Research Laboratory, The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract—Clay minerals and zeolites, candidate backfill minerals for nuclear waste repositories, were treated with saturated NaCl brine and Mg-rich (Mg-Ca-Na-K) brine at 200°C and 300°C for 4 weeks under a confining pressure of 30 MPa. The Al concentrations released in NaCl brine were lower than those in Mg-rich brine at both temperatures indicating that the Mg-rich brine is more acidic than the NaCl brine under these hydrothermal conditions. The Si concentrations in both brines were low because of the relatively acidic conditions developed during the hydrothermal treatment. As determined by X-ray powder diffraction or by specific Cs and Sr sorption measurements, no alteration could be detected in clay minerals treated with NaCl brine at 200°C. Among the zeolites tested, only phillipsite and erionite altered to analcime in NaCl brine at 200°C. Zeolites and most of the clay minerals tested did not alter in the Mg-rich brine treated at 200°C. Vermiculite altered to randomly interstratified vermiculite/K-vermiculite (mica-like) by selective K uptake from the Mg-rich brine.

At 300°C, the clay minerals did not greatly alter, whereas the zeolites altered to analcime and/or albite in the presence of the NaCl brine. In the Mg-rich brine, Al-rich montmorillonite from Wyoming did not alter, whereas Al-poor montmorillonite from Texas altered to randomly interstratified montmorillonite/illite at 300°C. Vermiculite collapsed to form K-vermiculite ($\sim 10.2 \text{ \AA}$) by the selective uptake of K from the Mg-rich brine at 300°C. Most of the zeolites altered to smectites in the Mg-rich brine at 300°C because of the acidic conditions generated by the hydrolysis of Mg. The selective Cs-sorption K_d decreased from 11,700 for untreated phillipsite to 240 and 15 for the hydrothermally produced analcime/albite mixtures from the phillipsite at 200° and 300°C, respectively, in NaCl brine. These results suggest that montmorillonites and mordenites are relatively more resistant than vermiculite or other zeolites at elevated temperatures and pressures in concentrated hydrothermal brines expected in a salt repository.

Key Words—Backfill, Bentonite, Cesium, Clinoptilolite, Hydrothermal, Mordenite, Salt repository, Smectite, Strontium, Vermiculite, Zeolite.

INTRODUCTION

Clay minerals and zeolites are candidate backfill minerals for nuclear waste repositories located in a variety of geological environments, such as salt, basalt, tuff, granite, and shale. The term backfill is applied to that material used to fill boreholes, mine shafts, and tunnels of a repository (see Gonzales, 1982, for details of a mined repository) when the repository is sealed. It has also been used to describe a possible component of the waste package in a multibarrier system of nuclear waste disposal. One concept of a waste package is given in Figure 1.

To distinguish between the 'backfill' used to fill mine shafts, tunnels, and boreholes and the 'backfill' of the waste package, the term 'overpack' has been used for the latter (see Komarneni and Roy, 1980). The terminology proposed by the U.S. Department of Energy (1980) does not distinguish between these two types of backfill; their terminology is illustrated in Figure 1. The overpack in Figure 1 is another canister made of an alloy such as TiCode 12 (ASTM grade 12 titanium, 0.8% Ni and 0.3% Mo), whereas the backfill is a mixture such as bentonite + sand. The primary functions of various types of backfill are: (1) to minimize or exclude the migration of groundwater between the host

rock and repository rooms or the waste canister system. (2) to control the Eh, pH, and chemical composition of the groundwater within the repository environment, and (3) to retard the migration of 'leaked' waste elements in the groundwater. The list of potential backfill materials includes expanding clays (bentonites), such as sodium or calcium montmorillonites, natural and synthetic zeolites, desiccants such as CaO and MgO, quartz sand mixed with bentonites, and powdered metals. These backfill materials may be used singly or in combination, and the nature of the backfill may vary with the geological formation.

In a salt repository, as in all potential repositories, geochemical interactions of the rock, backfill, and water may take place during the thermal period (Cohen, 1977). These interactions may take place under hydrothermal (hot, pressurized, and closed-system conditions) conditions (McCarthy *et al.*, 1978) during the thermal period. If backfill minerals which have been selected for their attractive sorptive and/or swelling properties alter by interaction with brine prior to leakage of radioactive ions, the very purpose of using them may be lost. The objective of this paper is to investigate the alteration of backfill minerals in simulated salt-repository brines under hydrothermal conditions. Brine inclusions in

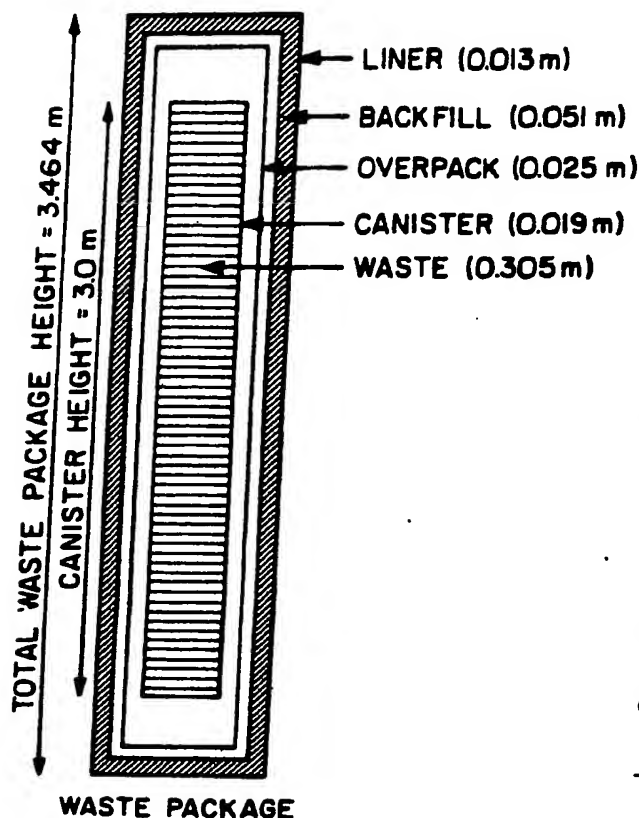


Figure 1. Waste package characteristics for commercial high level waste in a salt repository (draft interim reference repository conditions for commercial and defense high-level nuclear waste and spent fuel repositories in salt by The Reference Repository Conditions Interface Working Group, NWT-3, September 1981). According to the current designs, backfill for salt waste packages is a backup option.

halite as well as water in the backfill materials (clay minerals and zeolites) facilitate aqueous conditions in a salt repository. Closed-system experiments have been used in which the solid-liquid reactivity was investigated in gold capsules. Intrinsic variables such as Eh and pH varied with the bulk chemical composition and temperature conditions; however, no attempt was made to measure these two parameters. The redox potential, Eh is particularly difficult to control because gold is porous for H_2 generated (Komarneni, 1981) in the autoclaves. These experiments of short duration provide trends in the alterations of backfill barriers prior to the leakage of waste ions from canisters.

EXPERIMENTAL

Materials

Ten samples of clay minerals and zeolites (cation exchangers) were used in the present study. The source and/or location of all samples are given in Table 1. The montmorillonites were pulverized and homogenized by the supplier. These two standard montmo-

Table 1. Names, locations, sources, particle sizes of potential backfill samples.

Na-montmorillonite, Wyoming. SWy-1. Source Clays Repository, The Clay Minerals Society. Pulverized. Not size separated.
Ca-montmorillonite, Texas. STx-1. Source Clays Repository, The Clay Minerals Society. Pulverized. Not size separated.
Vermiculite, Poole property, Enoree, South Carolina. Zonolite Division, W. R. Grace and Company. 50-177 μm .
Phillipsite, Pine Valley, Nevada. Reference zeolite 27154. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Mordenite, Union Pass, Arizona. Reference zeolite 27134. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Mordenite, Lovelock, Nevada. Reference zeolite 27144. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Clinoptilolite, Castle Creek, Idaho. Reference zeolite 27034. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Clinoptilolite, Hector, California. Reference zeolite 27024. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Erionite, Shoshone, California. Reference zeolite 27104. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .
Chabazite, Christmas, Arizona. Reference zeolite 27124. Minerals Research, P.O. Box 591, Clarkson, New York. <75 μm .

illonites were used without size separation. The vermiculite sample was wet ground in a blender and sieved to obtain a 50-177- μm size fraction. The zeolites were supplied at -200 mesh (<75 μm) powders. X-ray powder diffraction (XRD) analysis of dried suspensions of the untreated samples was carried out with a Philips diffractometer using Ni-filtered $CuK\alpha$ radiation.

The Mg-rich brine and NaCl brine used here are similar to the brines for Waste Isolation Pilot Plant (WIPP) experiments. WIPP 'A' and WIPP 'B' brines respectively (Nowak, 1980).

Methods

To simulate the interactions of brines with backfills in a salt repository, 100 mg of each backfill mineral was loaded into a gold capsule. 200 μl of a Mg-rich brine (designated as NBT-6a brine and composed of 10% $MgCl_2$, 10% $CaCl_2$, 5% KCl , 5% $NaCl$ and 70% H_2O ; Mg-rich on a normality basis) or saturated NaCl brine was added, and the capsule was sealed by cold-welding (Komarneni *et al.*, 1979). The sealed gold capsules were treated hydrothermally in autoclaves at 200° and 300°C for 4 or 12 weeks under a confining pressure of 30 MPa.

After the hydrothermal treatment, the gold capsules were weighed to check the integrity of these closed-system type of experiments. The gold capsules devoid of any leaks were cut and opened with a scissors in a glass vial, 2 ml of distilled water was added while

washing the scissors, and then the gold capsules with samples were shaken to remove the sample from the gold capsule. The solid and solution phases were separated by centrifugation, and the solutions were analyzed for Si and Al by atomic emission spectroscopy (AES) using a computer-interfaced SpectraMetrics SpectraSpan III instrument. The solid samples were washed free of excess salt with water and 95% acetone, dried in an oven at 45°C, and subjected to XRD analysis to determine the mineralogical alterations produced by the hydrothermal treatments.

The XRD detection limit is too high to detect minor phases produced in the cation exchangers. More sensitive ways to detect alteration are total cation exchange or a selective cation-sorption measurement. Measurements of the total cation-exchange capacity are somewhat time consuming and not as relevant as selective cation-sorption measurements in the case of a salt repository because of the presence of large concentrations of Na⁺ and other ions. Therefore, selective cation-sorption measurements were made in this study. Selective Cs- and Sr-sorption is defined here as the amount of Cs and Sr ion exchange from a 0.04 N NaNO₃ solution. Twenty-five milliliters of 0.04 N NaNO₃ solution containing 0.0002 N CsCl and 0.0002 N SrCl₂ was added to either the untreated or hydrothermally altered samples, and the mixtures were equilibrated for 24 hr at 25°C. The solid and solution phases were separated by centrifugation. The amounts of Cs and Sr adsorbed were estimated by determining the Cs and Sr concentrations remaining in solution and reported as K_d values. K_d is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram of solid to the amount of Cs remaining per milliliter of the solution (see Tamura, 1972, for details of K_d). No replicates were used in the hydrothermal and ion-exchange studies. Cs in solution was determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer PE703 instrument with electrodeless discharge lamp. Strontium in solutions was determined by AES.

RESULTS AND DISCUSSION

Alterations of clay minerals and zeolites in saturated NaCl brine

The mineralogical alterations of clay minerals and zeolites under hydrothermal conditions of 200° and 300°C and 30 MPa pressure in NaCl are presented in Table 2. At 200°C, no alteration of the two montmorillonites and vermiculite could be detected in hydrothermal NaCl brine by XRD. Among the zeolites, phillipsite completely altered to analcime, whereas erionite altered to analcime only slightly in this brine at 200°C (Table 2). The high activity of Na⁺ in this brine drives the phillipsite – analcime reaction to the right (Taylor and Surdam, 1981). No mineralogical changes could

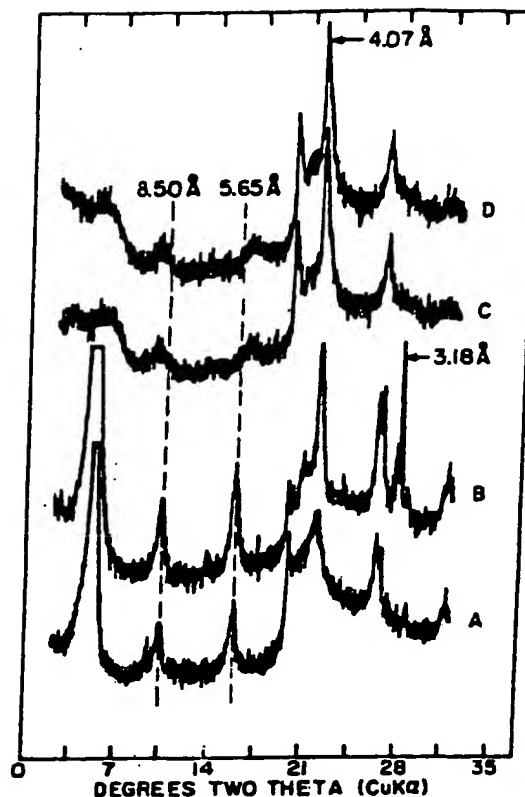


Figure 2. X-ray powder diffractograms of montmorillonite from Texas. (A) Ethylene glycolated; (B) Hydrothermally treated at 300°C/30 MPa/4 weeks in NaCl brine showing albite (3.18 Å); (C) Hydrothermally treated at 300°C/30 MPa/4 weeks in Mg-rich brine showing randomly interstratified montmorillonite/illite; (D) Same as (C) but after 12 weeks.

be detected in the mordenite, clinoptilolite, and chabazite samples when these zeolites were reacted with NaCl brine at 200°C and 30 MPa pressure. At 300°C, the Texas montmorillonite altered slightly to albite (Figure 2) but the Wymong montmorillonite did not. Vermiculite did not seem to change in this brine even after treatment at 300°C. Most of the zeolites transformed to analcime and/or albite (Table 2) at 300°C and 30 MPa pressure. This type of alteration was reported by Surdam (1977). The two mordenites and the Idaho clinoptilolite did not alter, probably because these zeolites are siliceous and siliceous zeolites are generally resistant to alteration (Breck, 1974).

Specific sorption of Cs and Sr by minerals treated hydrothermally in NaCl brine

Clay minerals and zeolites specifically exchange ions such as Cs and Sr; therefore, alteration of these materials can also be detected by a change in their selective sorption properties. Specific sorption of Cs and Sr by the various hydrothermally treated minerals is given in Table 3. Selective Cs sorption decreased only for phillipsite among all of the minerals that were hydro-

BEST AVAILABLE COPY

Table 2. X-ray diffraction analyses of untreated and hydrothermally treated minerals.

Sample ¹	Mineralogy of untreated samples	Mineralogical changes in saturated NaCl brine		
		200°C/30 MPa/4 wk	300°C/30 MPa/4 wk	300°C/30 MPa/4 wk
Montmorillonite, Wyoming	Montmorillonite, trace amounts of quartz, albite, mica, and calcite	No obvious change	No obvious change	No obvious change
Montmorillonite, Texas	Montmorillonite, trace amounts of cristobalite, quartz, K-feldspar, and talc	No obvious change	Montmorillonite, trace albite	No obvious change
Vermiculite, South Carolina	Vermiculite	No obvious change	No obvious change	No obvious change
Phillipsite, Nevada	Phillipsite	Analcite	No obvious change	Cristobalite, randomly interstratified montmorillonite/illite
Mordenite, Arizona	Mordenite	No obvious change	Albite, analcite	K-vermiculite (10.2 Å)
Mordenite, Nevada	Mordenite, cristobalite	No obvious change	No obvious change	Smectite, trace boehmite
Clinoptilolite, Idaho	Clinoptilolite	No obvious change	No obvious change	No obvious change
Clinoptilolite, California	Clinoptilolite	No obvious change	No obvious change	Cristobalite, mordenite
Erionite, California	Erionite	Erionite, analcite	Clinoptilolite, modified albite, analcite	Clinoptilolite, smectite
Chabazite, Arizona	Chabazite	No obvious change	Albite, quartz	Clinoptilolite, smectite
¹ Source, location listed in Table 1.				Smectite, unidentified phase (3.98 Å; 3.16 Å)
				Smectite, quartz

Table 3. Specific sorption of Cs and Sr as affected by the hydrothermal alteration of bakcfills in saturated NaCl brine.

Sample ²	Cs-sorption K_d ¹ (ml/g)			Sr-sorption K_d ¹ (ml/g)		
	untreated	200°C/30 MPa	300°C/30 MPa	untreated	200°C/30 MPa	300°C/30 MPa
Montmorillonite, Wyoming	410	400	510	170	200	310
Montmorillonite, Texas	310	685	740	310	370	370
Vermiculite, South Carolina	8900	10,100	990	2000	980	230
Phillipsite, Nevada	11,700	240	15	460	25	10
Mordenite, Arizona	8300	9500	7900	310	670	400
Mordenite, Nevada	6400	6700	30	170	370	25
Clinoptilolite, Idaho	3900	4800	5000	3000	6100	3500
Clinoptilolite, California	5600	5600	4600	4700	4700	590
Erionite, California	9500	11,700	40	490	590	40
Chabazite, Arizona	6600	8900	70	310	400	50

¹ K_d is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram to the amount of unsorbed Cs remaining per milliliter of the solution.

² Source, locations listed in Table 1.

thermally treated at 200°C because it altered to analcime (Table 2), a zeolite with ~ 2.2 -Å windows that does not easily exchange (Balgord and Roy, 1971) its cations. The Cs-sorption K_d decreased from 11,700 for untreated phillipsite to 240 for phillipsite treated at 200°C and 30 MPa pressure. With the rest of the minerals, specific sorption either remained the same or increased slightly. The increase of specific sorption by these minerals can be attributed to a change in the nature of the exchangeable ions in these minerals by the hydrothermal treatment in NaCl brine, i.e., the natural cations, such as K, Ca, and Mg in these minerals (for example, the Idaho clinoptilolite contained 4.23% Na₂O, 1.54% K₂O, and 0.60% CaO, whereas the Nevada phillipsite contained 5.12% Na₂O, 5.62% K₂O, and 0.10% CaO), were displaced by Na which competes less with Cs than either K or Ca or Mg (Ames, 1960, 1961, 1963; Tamura and Jacobs, 1961). The increased Cs sorption is a result of Na saturation of exchange sites and would be expected even at room temperature.

Specific Cs-sorption increased in both montmorillonites which were hydrothermally treated in NaCl brine

at 300°C presumably for the same reason as given above. The specific sorption K_d of Cs decreased from 8900 in the untreated vermiculite to 990 in the vermiculite which altered hydrothermally at 300°C probably because of partial chloritization by the hydrolysis of natural Mg²⁺ in the interlayers. XRD, however, did not reveal any mineralogical alteration, whereas specific Cs-sorption measurement indicated alteration of this mineral by hydrothermal treatment at 300°C. Specific Cs-sorption decreased (Table 3) with most of the zeolites which were hydrothermally treated at 300°C in NaCl brine because of transformation to analcime and/or albite. Specific Sr-sorption (Table 3) by the hydrothermally treated minerals closely paralleled that of the Cs sorption and can be explained similarly.

Alterations of clay minerals and zeolites in Mg-rich brine

The alterations of clay minerals and zeolites in Mg-rich brine under hydrothermal conditions are given in Table 2. The montmorillonites do not seem to alter in this brine at 200°C as detected by XRD. The vermic-

Table 4. Concentrations of Si and Al in the capsule fluids after hydrothermal treatments.

Sample ¹	Saturated NaCl brine				Mg-rich brine			
	200°C		300°C		200°C		300°C	
	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)
Montmorillonite, Wyoming	150	35	15	40	60	370	60	290
Montmorillonite, Texas	45	25	<1.3	35	50	360	80	280
Vermiculite, South Carolina	<1.3	<0.13	30	<0.13	25	180	20	<0.13
Phillipsite, Nevada	40	<0.13	6	<0.13	80	360	60	300
Mordenite, Arizona	35	90	10	120	65	380	40	290
Mordenite, Nevada	70	40	30	80	35	370	50	280
Clinoptilolite, Idaho	15	1	15	15	65	350	35	270
Clinoptilolite, California	50	15	<1.3	40	60	360	50	285
Erionite, California	70	45	60	95	65	380	60	310
Chabazite, Arizona	25	30	<1.3	120	80	380	60	320

¹ Source, locations listed in Table 1.

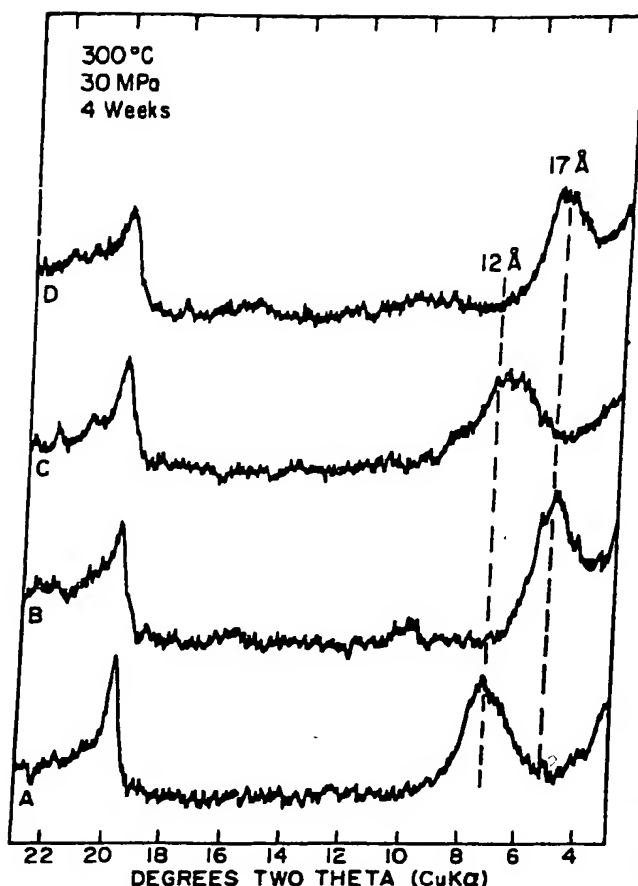


Figure 3. X-ray powder diffractograms of hydrothermal products of zeolites in Mg-rich brine. (A) 12-Å clay mineral formed from phillipsite, Pine Valley, Nevada; (B) Same as (A) but expanded to 17 Å upon exposure to ethylene glycol which indicated that it is smectite; (C) 12-Å clay mineral formed from chabazite, Christmas, Arizona; (D) Same as (C) but expanded to 17 Å upon exposure to ethylene glycol which indicated that it is smectite.

ulite which has a high layer charge (Komarneni and Roy, 1978) selectively adsorbed K from the Mg-rich brine (which contained substantial KCl) and transformed to randomly interstratified vermiculite/K-vermiculite (mica-like) with an average basal spacing of 12.6 Å. The transformation of vermiculite to K-vermiculite would decrease the cation-exchange capacity and selective ion sorption because interlayer K from K-vermiculite is not easily exchangeable. No alteration could be detected by XRD in any of the zeolites which were treated hydrothermally in this brine at 200°C.

Montmorillonite from Texas seemed to alter slightly in the Mg-rich brine at 300°C to cristobalite and randomly interstratified montmorillonite/illite (60:40) (Figure 2; Table 2). On the other hand, montmorillonite from Wyoming did not seem to alter by hydrothermal treatment at 300°C for 4 weeks (Table 2) or even after 12 weeks. The difference in reactivity be-

tween the two montmorillonites is not clear but may be attributed to a difference in their Al contents. Montmorillonite from Wyoming is more aluminous than the montmorillonite from Texas (van Olphen and Fripiat, 1979) and therefore the former is probably more stable than the latter under acidic conditions. The high-charge vermiculite collapsed to ~10.2 Å to form K-vermiculite by selective uptake of K⁺ ions from the Mg-rich brine. Zeolites, except for mordenites, altered to smectite (Table 2; Figure 3) in the Mg-rich brine at 300°C and 30 MPa pressure. This alteration is likely as a result of acidic conditions generated by the hydrolysis of Mg to form brucite (Komarneni, 1981). H⁺-saturation of the zeolite was probably followed by decomposition of the zeolitic framework and recrystallization to smectite. Experiments are presently underway to test this hypothesis of smectite formation. Acidic pH develops in highly saline solutions at elevated temperatures because of changes in hydrolysis constants and the association of ion-pair complexes, and the pH may decrease to about 3 in Mg-rich brine at 300°C (Claiborne *et al.*, 1980; Braithwaite and Molecke, 1980). Indirect evidence of the development of acidic conditions in the Mg-rich brine is provided by the release of substantial concentrations of Al into solution (Table 4) when these minerals were treated in the brines. More Al was released in the Mg-rich brine than in the NaCl brine under the same hydrothermal conditions because the Mg-rich brine is much more acidic than the NaCl brine (Braithwaite and Molecke, 1980). On the other hand, when these backfill candidates were treated under hydrothermal conditions the concentrations of Si in solution were very low in the acidic hydrothermal brines (Table 4) because silica is less soluble in acidic concentrations.

Specific sorption of Cs and Sr by minerals treated hydrothermally in Mg-rich brine

The specific sorption of Cs by all of the minerals treated hydrothermally decreased (Table 5) because of mineralogical alterations (Table 2) and/or change in the charge-balancing cations in these minerals. For example, K⁺ was selectively sorbed from the Mg-rich brine by the vermiculite, which collapsed to form K-vermiculite (randomly interstratified with vermiculite at this temperature). The formation of K-vermiculite led to a decrease in the specific Cs-sorption because interlayer ions in K-vermiculite are not easily exchangeable. Zeolites are also selective for K⁺ (Ames, 1961) and therefore, they may have been saturated with K⁺ during the hydrothermal treatment with the Mg-rich brine at 200°C. The K⁺ ions in the hydrothermally treated zeolites compete much better with Cs⁺ than the natural cations (mainly Na⁺, Ca²⁺, and K⁺) present in the untreated zeolites (Ames, 1960, 1961, 1963) and therefore, the selective Cs-sorption decreased at this temperature.

Table 5. Specific sorption of Cs and Sr as affected by the hydrothermal treatment of backfill in Mg-rich brine.

Sample ¹	Cs-sorption K_d ¹ (ml/g)			Sr-sorption K_d ¹ (ml/g)		
	untreated	200°C/30 MPa	300°C/30 MPa	untreated	200°C/30 MPa	300°C/30 MPa
Montmorillonite, Wyoming	410	—	180	170	—	250
Montmorillonite, Texas	310	350	160	310	270	170
Vermiculite, South Carolina	8900	7800	400	2000	440	130
Phillipsite, Nevada	11,700	4200	220	460	120	330
Mordenite, Arizona	8300	5100	6300	310	170	160
Mordenite, Nevada	6400	4400	2600	170	160	130
Clinoptilolite, Idaho	3900	2100	1700	3000	1400	270
Clinoptilolite, California	5600	3600	2900	4700	1400	200
Erionite, California	9500	5200	520	490	270	220
Chabazite, Arizona	6600	3100	200	310	310	250

¹ K_d is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram of solid to the amount of Cs remaining per milliliter of the solution.

² Source, locations listed in Table 1.

At 300°C, selective sorption of Cs⁺ by all of the minerals hydrothermally treated in the Mg-rich brine decreased (Table 5) because of the mineralogical alterations (Table 2). For example, K-saturation and collapse to form K-vermiculite drastically reduced the Cs sorption of the vermiculite sample. The Cs-sorption K_d decreased from 8900 in the untreated to 400 in the altered vermiculite. Zeolites such as phillipsite, erionite, and chabazite, altered almost completely to smectite in this Mg-rich brine and thus the overall Cs sorption did not decrease as much as it did when these zeolites altered in NaCl brine to form albite. Albite has little cation-exchange capacity, whereas montmorillonite has a substantial cation-exchange capacity and can selectively adsorb Cs (Tamura and Jacobs, 1961; Tamura, 1972). Phillipsite is interesting because at 300°C the smectite alteration product has about the same specific Cs-sorption capability as the untreated montmorillonites (Table 5). The specific sorption of Sr by the untreated and hydrothermally altered minerals seem to parallel the specific sorption of Cs at both the temperatures of hydrothermal treatment.

CONCLUSIONS

These data clearly illustrate relative stabilities, and the consequent changes in sorption capabilities of different candidate backfill materials under simulated repository conditions. Clay minerals and zeolites altered to various extents in either saturated NaCl brine or Mg-rich brine under hydrothermal conditions which may be expected in a salt repository for nuclear waste. Vermiculites altered to interstratified vermiculite/K-vermiculite or K-vermiculite (collapsed vermiculite) in brines containing K⁺. Most of the zeolites altered to analcime and/or albite in the saturated NaCl brine but altered to smectite in the Mg-rich brine. Montmorillonites and mordenites seem to be somewhat more resistant to alteration than the other candidate backfill materials and therefore, may serve as a good backfill in the waste package in a salt repository. Based on their

ion-sorption properties, zeolites would in general perform better at lower temperatures at some distance from the heat source; i.e., as a backfill for boreholes, mine shafts and tunnels, and both clay minerals and zeolites are likely to have applications in some portions of the repository tunnels and seal system.

ACKNOWLEDGMENT

This research was supported under subcontract E512-04200 with Battelle Project Management Division, Office of Nuclear Waste Isolation, under Contract No. DE-AC06-76-RL01830-ONWI with the U.S. Department of Energy.

REFERENCES

- Ames, L. L. (1960) The cation sieve properties of clinoptilolite: *Amer. Mineral.* 45, 689-700.
- Ames, L. L. (1961) Cation sieve properties of the open zeolites chabazite, mordenite, erionite, and clinoptilolite: *Amer. Mineral.* 46, 1120-1131.
- Ames, L. L. (1963) Mass cation relationships of some zeolites in the region of high competing cation concentrations: *Amer. Mineral.* 48, 868-882.
- Balgord, W. D. and Roy, R. (1971) Crystal chemical relationships in the analcime family. I. Synthesis and cation exchange behavior: in *Molecular Sieve Zeolites-1*. Adv. Chem. Ser., 101, Amer. Chem. Soc., Washington, D.C., 140-148.
- Braithwaite, J. W. and Molecke, M. A. (1980) Nuclear waste canister corrosion studies pertinent to geologic isolation: *Nucl. Chem. Waste Management* 1, 37-50.
- Breck, D. W. (1974) *Zeolite Molecular Sieves: Structure, Chemistry and Use*: Wiley, New York, 771 pp.
- Claiborne, H. C., Rickertsen, L. D., and Graham, R. F. (1980) Expected environments in high-level nuclear waste and spent fuel repositories in salt: *Report No. ORNL/TM7201*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 36 pp.
- Cohen, B. L. (1977) The disposal of radioactive wastes, from fission reactors: *Sci. Amer.* 236, 21-31.
- Gonzales, S. (1982) Host rocks for radioactive-waste disposal: *Amer. Sci.* 70, 191-200.
- Komarneni, S. (1981) Hydrothermal stability of β -Cs₂U₂O₇ and SrZrO₃ in fluids: *J. Inorg. Nucl. Chem.* 43, 2833-2837.
- Komarneni, S., Freeborn, W. P., and Smith, C. A. (1979)

- Simple cold-weld sealing of noble metal tubes: *Amer. Mineral.* 64, 650-651.
- Komarneni, S. and Roy, D. M. (1978) Effect of layer charge and heat treatment on Cs fixation by layer silicate minerals: *J. Inorg. Nucl. Chem.* 40, 893-896.
- Komarneni, S. and Roy R. (1980) Hydrothermal transformations in candidate overpack materials and their effects on cesium and strontium sorption: *Nucl. Tech.* 54, 118-122.
- McCarthy, G. J., White, W. B., Roy, R., Scheetz, B. E., Komarneni, S., Smith, D. K., and Roy, D. M. (1978) Interactions between nuclear waste and surrounding rock: *Nature* 273, 217-219.
- Nowak, E. J. (1980) Radionuclide sorption and migration studies of getters for backfill barriers: *Report No. SAND79-1110*, Sandia National Laboratories, Albuquerque, New Mexico, 54 pp.
- Surdam, R. C. (1977) Zeolites in closed hydrologic systems: in *Mineralogy and Geology of Natural Zeolites*, F. A. Mumpton, ed., Short Course Notes 4, Mineralogical Society of America, Washington, D.C., 64-91.
- Tamura, T. (1972) Sorption phenomena significant in radioactive-waste disposal: in *Underground Waste Management and Environmental Implications*, Amer. Assoc. Petrol. Geol. Memoir No. 18, Washington, D.C., 318-330.
- Tamura, T. and Jacobs, D. G. (1961) Improving cesium selectivity of bentonites by heat treatment: *Health Physics* 5, 149-154.
- Taylor, M. W. and Surdam, R. C. (1981) Zeolite reactions in tuffaceous sediments at Teels Marsh, Nevada: *Clays & Clay Minerals* 29, 341-352.
- U.S. Department of Energy (1980) Statement of position of U.S. DOE in the matter of proposed rule making on the storage and disposal of nuclear waste (waste confidence rulemaking). *U.S. Dept. of Energy Report No. DOE/NE-0007*, 212 pp.
- van Olphen, H. and Fripiat, J. J. (1979) *Handbook for Clay Materials and Other Non-Metallic Minerals*: Pergamon Press, Oxford, 346 pp.

(Received 30 August 1982; accepted 28 February 1983)

Резюме—Глинистые минералы и цеолиты, минералы, которые могут использоваться для засыпки хранилища ядерных отходов, были обработаны насыщенным соляным раствором NaCl и раствором, обогащенным Mg (Mg-Ca-Na-K), при температурах 200°C и 300°C в течение 4 недель в условиях поддерживаемого давления 30 МПа. Концентрации Al, освобожденного из раствора NaCl, были меньше, чем концентрации Al, полученные из растворов, обогащенных Mg, при обеих температурах. Это указывает на то, что растворы, обогащенные Mg, являются более кислотными, чем растворы NaCl в вышеописанных гидротермальных условиях. Концентрации Si в обоих растворах были низкие, потому что относительно кислотные условия создавались во время гидротермальной обработки. При помощи рентгеновской порошковой дифракции или измерений удельной сорбции Ca и Sr невозможно было обнаружить никаких изменений глинистых минералов, обработанных раствором NaCl в 200°C. Среди исследованных цеолитов только филлипсит и эрионит изменялись в анализим в растворе NaCl при 200°C. Цеолиты и большинство исследованных глинистых минералов не изменялись после обработки раствором, обогащенным Mg, при 200°C. Вермикулит изменялся в беспорядочно переслаивающийся вермикулит/К-вермикулит (слюда-подобный) путем селективного поглощения К из раствора, обогащенного Mg.

В температуре 300°C глинистые минералы особенно не изменялись, а цеолиты изменялись в анализим и/или альбит в присутствии раствора NaCl. В присутствии раствора, обогащенного Mg, при 300°C, монтмориллонит из Лаеминга, обогащенный Al, не изменялся тогда, как монтмориллонит, бедный Mg (из Тексаса), видоизменялся в беспорядочно переслаивающийся монтмориллонит/иллит. Вермикулит оседал и образовал К-вермикулит (~10,2 Å) путем селективного поглощения К из раствора, обогащенного Mg, при 300°C. Большинство цеолитов изменялось в смектиты, в растворе, обогащенном Mg, при 300°C в результате кислотных условий, созданных гидролизом Mg. Селективная Cs-сорбция K_d уменьшилась от 11700 для необработанного филлипсита до 240 и 15 для смеси анализим/альбит, гидротермально образованных из этого филлипсита в растворе NaCl при 200°C и 300°C соответственно. Эти результаты указывают на то, что монтмориллониты и мордениты являются относительно более сопротивляющимися, чем вермикулиты и другие цеолиты в условиях повышенных температур и давлений в концентрированных гидротермальных солевых растворах, ожидаемых в хранилищах. [E.G.]

Resümee—Tonminerale und Zeolithe, die beide für die Lagerung radioaktiver Abfälle verwendet werden, wurden mit gesättigten NaCl-Lösungen sowie Mg-reichen (Mg-Ca-Na-K) Salzlösungen bei 200° und 300°C über einen Zeitraum von 4 Wochen und einem Maximaldruck von 30 MPa behandelt. Die in die NaCl-Lösung abgegebenen Al-Konzentrationen waren geringer als die an die Mg-reiche Salzlösung abgegebenen Mengen. Dies wurde bei beiden Temperaturen beobachtet, was darauf hindeutet, daß die Mg-reichen Salzlösungen unter diesen hydrothermalen Bedingungen saurer sind als die NaCl-Lösungen. Die Si-Konzentrationen waren wegen der relativ sauren Bedingungen während der hydrothermalen Behandlung in beiden Salzlösungen gering. Wie mit Hilfe von Röntgenpulverdiffraktometrie und spezifischen Cs und Sr-Adsorptionsmessungen festgestellt wurde, trat bei den Tonmineralen unter der Einwirkung der NaCl-Lösung bei 200°C keine Umwandlung auf. Bei den untersuchten Zeolithen wandelten sich nur Phillipsit und Erionit in der NaCl-Lösung bei 200°C in Analcim um. Die Zeolithe und die meisten untersuchten Tonminerale zeigen in der Mg-reichen Lösung bei 200°C keine Umwandlung. Vermiculit wandelte sich in eine unregelmäßige Vermiculit/K-Vermiculit-Wechselagerung (glimmerähnlich) um, indem er K selektiv aus der Mg-reichen Salzlösung aufnahm.

Bei 300°C wandelten sich die Tonminerale kaum um, während sich die Zeolithe in der NaCl-Lösung in Analcim und/oder Albit umwandelten. In den Mg-reichen Lösungen veränderte sich der Al-reiche Montmorillonit von Wyoming nicht, wogegen sich der Al-arme Montmorillonit von Texas bei 300°C in eine unregelmäßige Montmorillonit/Illit-Wechselagerung umwandelte. Vermiculit kontrahierte bei 300°C zu K-Vermiculit (etwa 10,2 Å), indem er selektiv K aus der Mg-reichen Lösung aufnahm. Die meisten Zeolithe wandelten sich in der Mg-reichen Lösung bei 300°C in Smektiten um, da durch die Hydrolyse von Mg ein saures Milieu erzeugt wurde. Die selektive Cs-Adsorption, K_d nahm von 11700 für den unbehandelten Phillipsit bei den hydrothermal erzeugten Analcim/Albit-Mischungen auf 240 bzw 15 ab, die entweder bei 200° oder bei 300°C aus diesem Phillipsit in der NaCl-Lösung gebildet wurden. Diese Ergebnisse deuten darauf hin, daß Montmorillonit und Mordenit bei erhöhten Temperaturen und Drucken in konzentrierten hydrothermalen Salzlösungen, wie man sie bei der Lagerung in ehemaligen Salzlagerstätten erwarten kann, relativ widerstandsfähiger sind, als Vermiculit und die anderen Zeolithe. [U.W.]

Résumé—Des minéraux argileux et des zéolites, minéraux candidats pour le remplissage des dépôts de déchets nucléaires, ont été traités avec une saumure saturée de NaCl et avec une saumure riche en Mg (Mg-Ca-Na-K) à 200°C et 300°C pendant 4 semaines sous une pression confinante de 30 MPa. Les concentrations d'Al relâchées dans la saumure NaCl étaient plus basses que celles dans la saumure riche en Mg aux deux températures, indiquant que la saumure riche en Mg est plus acide que la saumure NaCl sous ces conditions hydrothermiques. Les concentrations de Si dans les deux saumures étaient basses à cause des conditions relativement acides développées pendant le traitement hydrothermique. On a déterminé par diffraction des rayons-X ou par mesures spécifiques de sorption de Cs et de Sr qu'aucune altération ne pouvait être détectée dans les minéraux argileux traités avec la saumure NaCl à 200°C. Parmi les zéolites examinées, seules la phillipsite et l'erionite se sont altérées en analcine dans la saumure NaCl à 200°C. Les zéolites, et la plupart des minéraux argileux examinés ne se sont pas altérés dans la saumure riche en Mg traitée à 200°C. La vermiculite s'est altérée en vermiculite/vermiculite-K (comme le mica) interstratifiée au hasard par prise sélective de K de la saumure riche en Mg.

A 300°C, les minéraux argileux ne se sont pas beaucoup altérés, tandis que les zéolites se sont altérées en analcine et/ou en albite en présence de la saumure NaCl. Dans la saumure riche en Mg, la montmorillonite riche en Al du Wyoming ne s'est pas altérée, tandis que la montmorillonite pauvre en Al du Texas s'est altérée en montmorillonite/illite interstratifiée au hasard à 300°C. La vermiculite s'est effondrée pour former une vermiculite-K (≈ 10.2 Å) par la prise sélective de K de la saumure riche en Mg à 300°C. La plupart des zéolites se sont altérées en smectites dans la saumure riche en Mg à 300°C à cause des conditions acides générées par l'hydrolyse de Mg. La sorption sélective de Cs, K_d , a diminué de 11700 pour la phillipsite à 240 et 15 pour le mélange analcine/albite produit hydrothermiquement à partir de la phillipsite à 200°C et 300°C, respectivement, dans la saumure NaCl. Ces résultats suggèrent que les montmorillonites et les mordenites sont relativement plus résistantes que la vermiculite ou d'autres zéolites à de hautes températures et pressions dans des saumures hydrothermiques concentrées attendues dans un dépôt salin. [D.J.]

THIS PAGE BLANK (USPTO)

BEST AVAILABLE COPY